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The effects of ferrocene concentration on soot in an ethylene laminar diffusion flame

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Metal fuel-borne catalysts are of interest in the combustion and environmental communities due principally to their ability to reduce carbon particulate mass emissions. However, a negative aspect to their use is the potential emission of the metals themselves. Post-combustion, these metals are usually in the form of ultrafine and nanoparticles. Particles emitted in this size range exhibit high degrees of dispersion, long atmospheric residence times, and an ability to be deeply inhaled into the lungs. In this study, ferrocene $[Fe(C_5H_5)_2]$ was doped in a laminar jet diffusion flame at varying concentrations to understand the mechanisms of particulate growth and chemistry. Ferrocene was used to effectively reduce the emissions of carbonaceous particulate matter was quantified using gravimetric analyses and an engine exhaust particle sizer (EEPS). At the point of carbonaceous particulate extinction, the flame is nonsmoking and only iron nanoparticles are emitted. Using gas chromatography-mass spectrometry, hydrocarbons and organic acids were extracted from the soot surface and quantified. Analysis of these organic compounds which had condensed on the surfaces of flame-generated particulate matter provide insights describing the properties of soot with varying degrees of ferrocene as well as the effectiveness of ferrocene to reduce organic emissions.

1. Introduction

Transition metals have been used as catalysts to reduce particulate emissions from combustion sources. Iron in the form of ferrocene has been one of the more widely studied compounds for its oxidative effects in laminar flame work. Bonczyk [1] used a laminar jet diffusion flame fueled by iso-octane to show many of the same results as others when ferrocene is seeded into the flame. Using 0.3% ferrocene by weight of fuel, it was clear that the smoke point of the flame had been raised because of the catalytic action of the iron. He also noted that iron increased the number density and particle size early in the flame, but caused a decrease in both during later stages of combustion in the flame (occurring in approximately the top third of the visible flame). Zhang and Megaridis [2] completed multiple studies on the effects of ferrocene when seeded into a laminar, co-annular, ethylene/air diffusion flame. They identified the regions in which the iron was reacting and incorporated into the carbon matrix of the soot agglomerates. At the level of doping used (0.35% weight ferrocene), occlusions of iron within the soot matrix were observed via transmission electron microscopy (TEM) from samples taken within the flame. They also noted that the smoke point of the flame had been raised considerably with the presence of ferrocene. In this case, evaluation of smoking was done by visually noting the qualitative quantity of black smoke (soot) emitted from the flame. Later, they expanded their work using the

same experimental approach. They measured line of site soot volume fractions using a He-Ne laser transmitting through the centerline of the flame[3]. This showed that ferrocene seeding leads to an acceleration of particulate inception, but has no effect on soot loadings where surface growth dominates the sooting process. At the tip of the flame, there was a noticeable decrease in soot volume fraction and mean particle size due to the presence of the iron. These findings confirm that the presence of ferrocene alters the smoke point of the flame.

Yang [4] also used a co-annular diffusion flame burner to show iron's ability to inhibit soot. The main fuel utilized was ethylene gas with supplementary acetylene to further increase soot production. Instead of using ferrocene, he used iron pentacarbonyl with similar catalytic results. With TEM they also observed that the liberated iron was not spherical, but a rigid crystalline polygon.

Contrary to what is observed in laminar diffusion flames, the addition of ferrocene to a premixed flame has been shown to increase soot volume fractions near the end of the flame tip. Sarofim *et al.* at MIT demonstrated this and theorized that it was due to the rapid nucleation at the base of the flame with continual soot growth to the later stages in the flame [5,6]. This research showed that the catalytic properties of the iron could not overcome the soot growth in a premixed flame.

2. Experiment

For this study a laminar, co-annular jet diffusion flame was utilized. The design of the burner is described by Santoro *et al.* [7] with an alteration of glass beads being omitted from the fuel tube. Ethylene gas (99.9% purity) was utilized as the sole fuel source with a flow maintained at 0.294 L/min. The co-flowing oxidizer of dried, HEPA filtered air had a flow of 64.0 L/min set by a mass flow controller. Varying concentrations (0-1050 ppm iron by mass) of ferrocene were doped into the fuel based on the temperature-partial pressure relationship described by Jacobs *et al.* [8]. Two fuel lines controlled independently with separate mass flow controllers ran through coils within a water bath set to 343 K. Outside of the water bath, the lines were wrapped in heating tape at 373 K and teed together to form one fuel line leading to the burner cup. One of the fuel lines (prior to the tee) was kept free of ferrocene, a 15.9 mm stainless steel tube that follows the coil in the bath was packed with alternating layers of 1.5 mm glass beads and ferrocene with glass wool stuffed at the ends of the cylinder. This allowed the flow of ethylene to become fully saturated with ferrocene. The proportionality of the total 0.294 L/min that flowed through the doped fuel line determined how much iron is part of the combustion process.

3. Results

3.1 Particulate Physical Characteristics

Initial experiments showed that the introduction of iron into the flame (1050 ppm) changes the flame from a smoking flame to a non-smoking flame. From visual inspection, the addition of iron to the system clearly reduces the amount of soot being emitted from the flame. Also, the transition from a smoking flame to a non-smoking flame produces a well-defined, non-flickering tip. Size distribution measurements of particulate matter using a Engine Exhaust Particle Sizer (EEPS) were taken at seven different doping levels, ranging from undoped to 840 ppm of iron. The only parameter that was changing over the course of these tests was the quantity of ferrocene being introduced to the flame. As can be seen in Fig. 1, when iron increases, the peak located at 140 nm decreases. This trend holds true until the flame becomes non-smoking beyond concentrations of 525 ppm. Any further doping results in a growing peak at 10 nm (Fig. 1b).

The large peak at 140 nm, corresponding to the accumulation mode, is comprised of carbon agglomerations with iron being incorporated into the carbon matrix with any level of doping [9]. The resulting nano-regime from the non-smoking flame is from liberated iron particles. This confirms what is observed through the use of TEM by Zhang and Megaridis [2, 3] at higher levels of doping (1050 ppm iron or 3500 ppm of ferrocene). The appearance of this peak is due to the liberation of iron in the flame. The excessive iron catalyst within the flame aids in burning all of the soot prior to emission. This leaves liberated iron nanoparticles as the main source of PM emission.

As the accumulation mode shrinks with the addition of ferrocene, the total concentration of particles emitted decreases as well as seen in Fig. 2. The total number concentration of PM only increases with the addition of ferrocene when the PM emitted is dominated by iron primary particles in a non-smoking flame.



Figure 1- (a) Size distribution; (b) Size distribution near smoke point

Flame exhaust was pulled over Teflon membrane filters (2.0µm pore size) in triplicate (*i.e.*, gravimetric analysis) at four different flame doping levels: 0 ppm, 160 ppm, 420 ppm, and 700 ppm. As more iron is added to the flame, the particulate mass emissions decrease. This is due to the carbonaceous emissions being further oxidized because of the catalytic presence of iron. The amount of iron being added to the flame is small compared to the amount of soot being produced at lower levels of doping. It can be seen in Fig. 3 that when iron nuclei are solely being emitted from the flame (seen at 700 ppm iron) that the particulate mass emitted is significantly less than when carbonaceous soot is emitted. This shows that continual addition of ferrocene significantly reduces the overall mass emissions without adding much mass from the iron itself. In a pure diffusion flame such as this, it shows that there is a theoretical optimal doping level in which the addition of ferrocene eliminates the agglomerates of carbon and iron at 140 nm while not contributing to formation of iron primary particles at 10 nm.

3.2 Particulate Chemical Characteristics

Particulate emitted from seven different concentrations of iron concentrations in the flame were collected on 47 mm quartz fiber filters. The filters were rinsed with a HIB solution (40% hexane, 40% benzene, and 20% isopropanol) to extract the organics condensed on the surface of the PM. The rinse was concentrated and run on an Agilent 6890 gas chromatograph equipped with a low resolution 5973 mass selective (GC/MS) detector with the purpose of identifying alkanes and

polycyclic aromatic hydrocarbons (collectively, HCs). After methylating an aliquot of the concentrated rinse with diazomethane, the sample was run on the same GC/MS for organic acids (OAs). Internal standards of deuterated compounds were spiked into samples run on the GC/MS. As can be seen from Table 1, any amount of iron less than or equal to 420 ppm resulted in "non-detects." All quantities less than the detection limit are considered "non-detects." The lack of HCs extracted is likely due to the nature of simple diffusion flames. The soot produced by an undoped diffusion flame with a neat sooty fuel produce a flame that is very low in organic carbon. It has been shown that less than 10% of the carbon associated with a flame such as this is organic carbon[10].



Figure 2 - Total Particle Concentration

Figure 3 - Mass Concentration

The very high carbon content of the flame-generated soot may act as an activated carbon filter holding onto the HCs via adsorption. This adsorption is caused by van der Waals forces. The extraction technique used to attempt to dissolve the chemicals condensed on the surface of the soot did have the ability to overcome the van der Waals forces. The internal standard spike recovery from these tests also turned out very low. With doping concentrations from 0 ppm to 420 ppm all of the recovery spikes were less than 25% of their expected values. The other three samples had better recoveries, but still not to an amount that gives much confidence to the effectiveness of the extractions (range from 90% to 0% with most between 30-60%). This could greatly contribute to having HC non-detections. As the amount of carbon decreases with the increased presence of ferrocene, HCs are found to be more readily available for analysis and ensure the sample is above the detectability limits of the process.

Concentrations of specific organic acids (OA) are found in Table 2. As can be seen in this table, as more iron was incorporated into the flame, the concentrations of OAs decreased. In the four lowest quantities of iron incorporation, it is seen that the OAs have greater concentrations by over three orders of magnitude compared to the highest concentrations of HCs extracted. When the total concentrations of OAs extracted for 700 ppm and 1050 ppm iron are compared to the concentrations of HCs for the same level of doping, there is only about a single order of magnitude of difference $(2.13\mu g/m^3 \& 2.55 \ \mu g/m^3 \ compared to 0.40 \ \mu g/m^3 \& 0.13 \ \mu g/m^3$, respectively). This lends further support to the theory that the more carbonaceous emissions are acting as a carbon filter by adsorbing the HCs and not releasing them during the extraction process.

Organic acids are not as readily adsorbed by carbon filters due to their hydroxyl group. Because of this, the OAs are more easily extracted from the surface of the carbon soot. This is seen by the

orders of magnitudes of difference in concentrations extracted between OAs and HCs. When the amount of available carbon for adsorption decreases with the increase in iron introduced into the fuel, a more indicative value of HCs can be seen. The relative similarity in values of total OAs and HCs found at the two highest levels of fuel doping indicates this. It is observed that the concentration of OAs extracted from the particulate surface considerably decreases at 525 ppm and greater (near the transition where iron nanoparticles are the solely emitted PM).



Figure 4 – OA and HC Concentrations at Different Levels of Doping

While completing the previously described GC/MS work, some noticeable peaks appeared on the spectrum that were attributed to compounds which were not initially sought. The presence of these compounds contributed to a mechanism of combustion that will be later discussed. Some of these compounds frequently identified in the flame are: benzaldehyde, benzoic acid, phenol, and biphenyl. At the highest doping rate (1050 ppm) of iron in the flame there is residual unburned ferrocene in the exhaust at 0.1174μ g/m³(estimated based on nearest internal standard response). In this instance the ferrocene is being doped into the flame with such excess that some of it is getting through the flame without being combusted as a catalyst or being oxidized in the flame to produce iron nuclei.

4. Conclusions

The addition of ferrocene to the laminar jet diffusion flame acted as expected by reducing the number and mass of soot particulate. The ferrocene acted as a catalyst in oxidizing the soot and fuel, the more ferrocene added to the flame the more it aided in oxidation to the point that virtually all hydrocarbons and soot had been oxidized. This critical correlation was observed near 525 ppm of iron doping. At this point, minimal carbonaceous matter was emitted from the flame because of the effect of ferrocene. Furthermore, the amount of ferrocene is enough for the soot to be oxidized fully, but there was a minimal amount of iron primary particles emitted. Any doping beyond this point only increases the amount of iron nuclei emitted.

HC and OA extractions from flame PM resulted in inefficient quantifying of HCs at low levels of fuel doping. This inefficiency and inability to recover HC standards used in the extraction process demonstrated that soot produced with low levels of iron fuel-borne catalysts create soot that is composed almost entirely of elemental carbon. The soot acts in the same way an activated

carbon filter would by adsorbing the HCs to its surface. The solvent rinses used for the extractions did not have the ability to pull these adsorbed HCs from the surface. Because of this, iron doping concentrations between 0 ppm and 420 ppm produced non-detections for all HCs attempted for the GC-MS work.

The OAs extracted from particulate matter changed by a factor of 165 between 700 ppm to 0 ppm $(351.28 \ \mu g/m^3 \text{ to } 2.13 \ \mu g/m^3)$ of doping. When this factor is compared to the factor of change in mass between these to two levels of doping, there is a noticeably larger change in OAs (165 to 93). The difference in these ratios can be attributed to two different causes. Primarily, the presence of the iron catalyst causes preferential oxidizing of OAs compared to the overall mass of particulate, revealing the nature of catalytic ferrocene. Secondly, the ability for OAs to condense on the particulate's surface is limited by the available surface area. From 0 ppm to 700 ppm, the surface area changes by a factor of 200 (conservatively assuming all particles are spherical). This shows that increasing iron concentrations effect surface area by a greater factor than overall mass emissions and thus possibly limiting the amount of OAs that can condense on the surface area.

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